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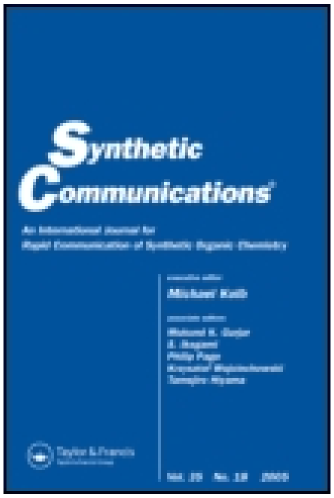

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Silica-Acetate Complex of N_2O_4: A Heterogeneous Reagent for the Selective Nitration of Phenols and Nitrosation of Thiols

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Silica-Acetate Complex of N_2O_4: A Heterogeneous Reagent for the Selective Nitration of Phenols and Nitrosation of Thiols

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ABSTRACT

Complexation of gaseous N_2O_4 with acylated silica gel affords an addition compound, which is an efficient heterogeneous reagent for the selective mono- and dinitration of phenol, substituted phenols and nitrosation of thiols.

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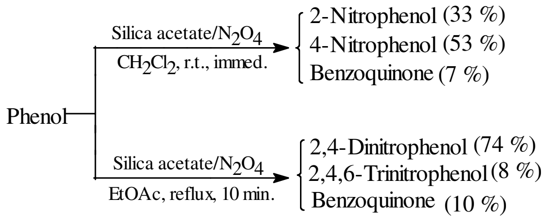
There are many important synthetic transformation such as nitration, nitrosation, oxidation, and oxidative cleavage reactions which are performed with gaseous dinitrogen tetroxide.[1–13] The reactions with this reagent usually suffer from high reactivity of the reagent and needs to be carefully controlled by lowering the reaction temperature[14–16] to avoid side reactions. Molecular addition compounds of N_2O_4 gas with some oxygen containing organic compounds such as 1,4-dioxane or 18-crown-6 have been also prepared and their structures have been elucidated.[17,18] Recently, we reported on the application of 18-crown-6 complex of N_2O_4 for nitration of phenols and also nitrosation of thiols.[19,20] In comparison with the gaseous N_2O_4, the use of 18-crown-6/N_2O_4 complex has some reported advantages over N_2O_4, but the remained problems with this complex is that 18-crown-6 is relatively an expensive precursor and its N_2O_4 complex is very soluble in organic solvents. Due to the solubility of this complex in organic solvents, in the work-up procedure, chromatography is required. Especially, in the case of in situ synthesis of unstable thionitrites from thiols, the presence of soluble 18-crown-6/N_2O_4 in the reaction mixture does not let to have a pure solution of thionitrites for further synthetic applications.

Recently we introduced silica-acetate/N_2O_4 complex and used it for selective oxidation of sulfides.[21] Now, we report on the application of this cheap and easily prepared solid complex as a heterogeneous reagent for selective mono- and dinitration of phenol, substituted phenols and nitrosation of thiols.

We first optimized the reaction conditions for the nitration of phenol. We observed that in the presence of this reagent in CH_2Cl_2, the reaction goes to completion immediately with the formation of *ortho*- and *para*-nitrophenol in 33% and 53% respectively. When this reaction was refluxed in ethyl acetate in the presence of 2 molar equivalents of the reagent, the reaction furnished 2,4-dinitrophenol in 78% together with the formation of 2,4,6-triphenol in 8% yields. The formation of some quinone in the nitration reaction of phenol with N_2O_4 or its organic and inorganic complexes is inevitable and here is also some of it formed[19,23] (Sch. 1).

We then used this reagent for the nitration of different substituted phenols. The mono- and dinitration reaction of phenols having different halogens, methyl and acetyl as substitutes were performed selectively under different reaction conditions. The mono-nitration reactions performed in CH_2Cl_2 at room temperature, while; dinitration reactions proceeded in refluxing ethyl acetate. The results are shown in Tables 1 and 2.

Although the use of heterogeneous reagents such as ‘claycop’ and ‘clayfen’ (clay impregnated with copper nitrate and ferric nitrate, respectively) have been used for nitrosation of thiols,[22] but, the produced



Scheme 1.

Table 1. Mononitration of substituted phenols with one molar equivalents of silica-acetate/N_2O_4 in CH_2Cl_2 at r.t.

Entry	Substrate	Time (min)	Product (isolated %)
1	4-Fluoro-	5	4-Fluoro-2-nitro- (91)
2	4-Chloro-	5	4-Chloro-2-nitro- (95)
3	4-Bromo-	10	4-Bromo-2-nitro- (90)
4	4-Methyl-	5	4-Methyl-2-nitro- (86)
5	4-Acetyl-	10	4-Acetyl-2-nitro- (88)
6	2,6-Dichloro-	5	2,6-Dichloro-4-nitro- (96)
7	2,6-Dimethyl-	5	2,6-Dimethyl-4-nitro- (83)

Table 2. Dinitration of substituted phenols with two molar equivalents of silica-acetate/N_2O_4 in reflux conditions.

Entry	Substrate	Solvent	Time (min)	Product (isolated %)
1	4-Fluoro-	EtOAc	30	4-Fluoro-2,6-dinitro- (94)
2	4-Chloro-	EtOAc	45	4-Chloro-2,6-dinitro- (96)
3	4-Bromo-	EtOAc	45	4-Bromo-2,6-dinitro- (83)
4	4-Methyl-	EtOAc	20	4-Methyl-2,6-dinitro- (95)
5	4-Acetyl-	BuOAc	30	4-Acetyl-2,6-dinitro- (74)

thionitrite is immediately oxidized into the corresponding disulfides by the copper and iron ions present in the reagents. Similarly, the use of $Cu(NO_3)_2{\cdot}N_2O_4$[23] and $Fe(NO_3)_3{\cdot}1.5N_2O_4$[23] for nitrosation of thiols suffer from the over-oxidation of the obtained thionitrite into their corresponding disulfides.

In order to overcome the problems encounter in the conversion of thiols into thionitrites under homogeneous conditions and having the possibility of performing the reaction under heterogeneous conditions, we used successfully silica-acetate/N_2O_4 complex for this purpose (Sch. 2).

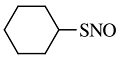
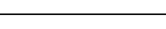
This reagents converted structurally different thiols into their corresponding thionitrites without the formation of any disulfide or over-oxidized products in solvents such as diethyl ether, dichloromethane, ethyl acetate or *t*-butanol at room temperature. The use of *t*-butanol as the solvent of the reaction has the advantageous that after filtration of the insoluble reagent, the obtained pure solution of thionitrite can be solidified by keeping it in a fridge and stored without any change for days. The obtained thionitrites were characterized on the basis of their UV spectral data and comparison with the literature[15,16] (Table 3).

In conclusion, the use of silica-acetate/N_2O_4 complex provides the possibility of performing the selective mono- and dinitration of phenols and also nitrosation of thiols under heterogeneous conditions. The ease of preparation, handling and cheapness of the reagent, heterogeneous

$$\mathrm{RSH} \xrightarrow[t\text{-butanol , r.t.}]{\text{Silica-acetate/N}_2\text{O}_4} \mathrm{RSNO}$$

Scheme 2.

Table 3. Reaction of thiols (R–SH) with silica-acetate/N_2O_4 in *t*-butanol at room temperature.[a]

Entry	*R*	Product[b]	λ_{max} (nm)/absorbance
1	*n*-Bu	$CH_3(CH_2)_2CH_2SNO$	338.3/2.16, 552/0.27
7	*n*-Pr	$CH_3CH_2CH_2SNO$	341.9/1.71, 598.2/0.15
8	$PhCH_2$	$PhCH_2SNO$	342/1.94, 551.8/0.11
2	Ph	PhSNO	368.9/0.95, 572/0.22
3	Cyclohexyl		339/0.87, 553.4/0.19
4	*n*-Octyl	$CH_3(CH_2)_6CH_2SNO$	339.6/2.11, 551/0.16
5	Et	CH_3CH_2SNO	337.5/1.76, 551.8/0.13
6	$–CH_2CH_2CH_2–$		340/1.65, 550.2/0.18

[a] The reaction occurs immediately.

[b] The products are identified by comparison of their UV spectral data with the literature.[15,16]

nature of the reactions and ease of the work-up, and the possibility of obtaining pure solution of thionitrites can be considered as advantageous of this reagent.

EXPERIMENTAL

Thin layer chromatography on commercial plates of silica gel 60 F_{254} was used to monitor the progress of the reactions. Column chromatography was carried out using silica gel 60. All the products of nitration reactions are known compounds and were characterized by comparison of their physical and spectral data with authentic samples. Thionitrites were identified in the solution and characterized by comparison of their UV spectral data with literature. UV spectra were recorded on Pye Unicam 8725 spectrometer. IR spectra were recorded on a Perkin Elmer 781 spectrometer. NMR spectra were recorded on a Bruker DPX 250.

Mononitration of Phenol with Silica-Acetate/N_2O_4 Complex

A mixture of phenol (0.094 g, 1 mmol) and silica-acetate/N_2O_4 complex (1.2 g) in CH_2Cl_2 (4 mL) was stirred vigorously at room temperature. The reaction completed immediately. Acetone (5 mL) was added and the mixture was filtered. The resulted mixture was presorbed on silica gel (5 g) and was applied on a silica gel column and eluted with peroleum ether/acetone (9:1). 4-Nitrophenol 0.069 g, 53%, m.p. 112°C, [Lit.[24] m.p. 112–114°C], 2-nitrophenol 0.043 g, 33%, m.p. 45°C, [Lit.[24] m.p. 45–46°C] and benzoquinone 0.008 g, 7%, m.p. 113°C, [Lit.[24] m.p. 112.5–113.5°C] were obtained respectively.

Dinitration of Phenol with Silica-Acetate/N_2O_4 Complex

A mixture of phenol (0.094 g, 1 mmol) and silica acetate/N_2O_4 complex (2.5 g) in EtOAc (5 mL) was stirred for 10 min. under reflux conditions. Acetone (5 mL) was added and the mixture was filtered. The resulted mixture was presorbed on silica gel (5 g) and was applied on silica gel column and eluted with chloroform as an eluent. 2,4-Dinitrophenol 0.136 g, 74%, m.p. 111°C, [Lit.[24] m.p. 111–113°C, 2,4,6-trinitrophenol

0.018 g, 8%, m.p. 120–122°C, [Lit.[24] m.p. 121–122°C] and benzoquinone 0.01 g (10%) were obtained respectively.

Mononitration of 4-Chlorophenol with Silica-Acetate/N_2O_4 Complex as a Typical Procedure

A mixture of 4-chlorophenol (0.129 g, 1 mmol) and silica-acetate/N_2O_4 complex (1.2 g) in CH_2Cl_2 (4 mL) was stirred vigorously at room temperature for 5 min. Acetone (5 mL) was added and the mixture was filtered. The resulted mixture was presorbed on silica gel (5 g) and was applied on silica gel column and eluted with peroleum ether/acetone (9:1). 4-Chloro-2-nitrophenol 0.164 g, 95%, m.p. 90°C, [Lit.[25] m.p. 91°C] was obtained as yellow needle crystals.

Dinitration of 4-Chlorophenol with Silica-Acetate/N_2O_4 Complex as a Typical Procedure

To a solution of 4-chlorophenol (0.129 g, 1 mmol) in EtOAc (5 mL), silica-acetate/N_2O_4 complex (2.5 g) was added. The mixture was refluxed for 45 min. Aceton (5 mL) was added and the mixture was filtered. The resulted mixture was presorbed on silica gel (5 g) and was applied on silica gel column and eluted with peroleum ether/acetone (8:2). 4-Chloro-2,6-dinitrphenol was obtained, 0.20 g, 96%, m.p. 80°C, [Lit.[26] m.p. 81°C].

Nitrosation of Thiophenol with Silica-Acetate/N_2O_4 Complex as a Typical Procedure

To a solution of thiophenol (0.11 g, 1 mmol) in *t*-butanol (5 mL), silica-acetate/N_2O_4 complex (1.2 g) was added. The resulting mixture was stirred at room temperature. The reaction was completed immediately and a bright red solution was obtained. This mixture can be froze and kept for several days without any change.

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